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ORIGIN OF THE SEGMENTAL COLORATION OF AMETHYST AND SMOKY QUARTZ

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DESCRIPTION OF THE SEGMENTAL COLORATION

The pseudo-racemic twinning and the pigmentation of the amethyst variety of quartz have been the occasion of numerous studies,[1] but many questions concerning these characteristics of the variety have not as yet been answered, among which is that of the origin of the sectoral distribution of color commonly seen in cut basal sections. This feature, early remarked on and figured by Brewster (1823), and by many of the subsequent workers, is seen as three colored radial triangular sectors based upon alternate faces of the hexagonal prism which bounds such sections and alternating with three uncolored triangular sectors. When the six sectors are symmetrical and of equal size, their apices meet at the center of the section, but it is usually found that the three uncolored triangular sectors are subordinate in size and occupy the marginal portion of the section but with their altitudes, when extended, still meeting at the center. The colored sectors in such instances have a seven-sided outline, the interior apical angle being 120°. In some instances only three (colored) sectors are present, each of 120° at the apice. Occasionally it is found that all six of the sectors are amethystine, but generally of a lighter shade in the smaller sectors, or that the smaller sectors have a citrine or smoky color, the sectorally distributed amethyst color appear-

[1]Among which can be mentioned those of Brewster (1823), Marx (1831), Rose (1844), Haidinger (1845–1854), Dove (1853), Descloizeaux (1855), vom Rath (1874), Groth (1877), Böklen (1883), Judd (1888, 1893), Lacroix (1901), Tutton (1911, 1924), Raman and Banerji (1925) and Mügge (1932) on the twin structure and optical behavior, and of Rose (1800). Heintz (1843), Rammelsberg (1875), Weinschenk (1896, 1900), Kraatz-Koschlau and Wöhler (1899), Nabl (1899, 1900), Hermann (1908), Doelter (1908–1915), Watson and Beard (1917), Wild, and Wild and Liesegang (1922–1932), Holden (1923, 1925) and Klemm (1925, 1927), among others, on the pigmentation.

ing to be superposed on a uniform citrine or smoky coloration. A further well known peculiarity in connection with the sectoral coloration is in that the pseudo-racemic twinning characteristic of the variety is found chiefly in the colored sectors. A photograph of a sectorally colored amethyst is given in Fig. 1 and of a sectorally colored smoky quartz crystal in Fig. 2. Photographs and drawings of the color distribution and of the twin structure are also given by Tutton (1911, 1924), Judd (1893) and Brauns (1903).

When entire crystals are examined it is seen that the sectoral coloration of basal sections is present as a segmental coloration in the whole, the pigment being disposed in regions or segments of the crystal subjacent to certain of the growth faces and extending inward with diminishing size to the center or original nucleus of the crystal. When the crystals are examined more closely it is seen that the pigment present in the colored segments is generally distributed in thin and closely spaced layers or planes parallel to the growth faces bounding each particular segment. Crystals whose colored segments do not exhibit color planes, or in which the color planes are too thin and too closely spaced to be discernible, are uncommon. In very light colored crystals the color planes may be widely spaced, several millimeters or more apart, and may be seen then only by orienting the crystal so as to view the trace of the plane. This distribution of the color in planes and interior segments related to the growth surfaces is consistent with the idea that the pigmenting substance was included by the crystal during its growth. The color of amethyst is occasionally distributed quite irregularly within the crystal. Amethysts otherwise evenly colored sometimes contain small irregularly bounded regions of a very intense color, and colorless crystals may be similarly pigmented. Schoolcraft (1824) says of an occurrence of smoky quartz at Keewiiweenon Point, Michigan Territory, that "The colour is not equally intense, but often appears in clouds, and is mingled with the violet hue of the amethyst" and of amethyst from the same locality as "Its colour passes from violet to purple, and is seldom uniformly diffused. It is intimately connected with the preceding variety (smoky quartz), and the colours so mingled, in some pieces, as to make it difficult to determine to which sub-species they ought to be placed." Color planes parallel to the growth faces are usually discernible, however, within such irregularly colored regions. The apical parts of the rhombohedral faces of amethyst are quite generally more deeply colored than the remainder of these faces. The distribution of color in amethyst has also been described by Wild and Liesegang (1923).

Study of a commercial stock of uncut amethysts[1] and of a suite of amethyst and smoky quartz crystals in the collection of The American Museum of Natural History, including a number of sectioned crystals, has brought out that, of the three forms—$(10\bar{1}1)$, $(01\bar{1}1)$ and $(10\bar{1}0)$—commonly present on quartz crystals, the three faces of the terminating positive rhombohedron $(10\bar{1}1)$ invariably contain pigmented segments beneath them and that it is these segments that when exposed in a basal section yield the sectoral coloration seen therein. Of the two remaining forms the terminating negative rhombohedron $(01\bar{1}1)$ is found to frequently occur with colored segments beneath its faces while the prism $(10\bar{1}0)$ less frequently occurs so. Crystals colored by $(01\bar{1}1)$ alone were not observed, although crystals colored by $(10\bar{1}1)$ are common, and when the former contains colored segments it is found to do so only in conjunction with $(10\bar{1}1)$. When $(10\bar{1}0)$ occurs colored it is found so usually in conjunction with both $(10\bar{1}1)$ and $(01\bar{1}1)$, although the combination of $(10\bar{1}0)$ and $(10\bar{1}1)$, with $(01\bar{1}1)$ uncolored, was met with in a few instances. Crystals in which all three of the forms are present and are uniformly colored are rare. When two or all three of the forms are colored it is frequently noted that the color is most intense in the segments belonging to $(10\bar{1}1)$. It is difficult to observe such a difference in intensity of coloration, however, particularly when the faces of one form, usually those of $(10\bar{1}1)$, are large in comparison with the others, except by sectioning or fracturing the crystal. Uniformly colored amethyst crystals are commonly found to have a pyramidal habit, the prism $(10\bar{1}0)$ being absent, and this habit seems to be particularly common with more deeply colored crystals. Several instances were observed of crystals in which both $(10\bar{1}1)$ and $(01\bar{1}1)$ had included pigment during the early stages of their growth but in which $(01\bar{1}1)$ had, during a later stage of growth, abruptly stopped including pigment on its faces while $(10\bar{1}1)$ continued to do so.

The peculiarities of coloration and of the size and distribution of the sectors of basal sections are all explainable by considering the habit of the sectioned crystal, the identity of the colored and uncolored segments, and the point, with reference to the original nucleus of the crystal, at which the section intersects the colored segments. In basal sections cut through the rhombohedral faces of a crystal bounded by the three common forms and in which $(10\bar{1}1)$ is selectively colored, the colored and uncolored sectors are the horizontal projections of the terminating rhom-

[1]Through the courtesy of Mr. M. B. Hanauer of the American Gem and Pearl Co., New York City, to whom the writer is also indebted for a gift of specimens.

bohedral faces, but in sections cut from near the base of the same crystal the sectoral portion is smaller, although the sizes of the sectors are still in the same ratio as the sizes of the terminating faces, and it is located in the interior of the section. The latter sections may then be bordered by a uniformly colored or uniformly colorless zone according to whether the segments below the prism $(10\bar{1}0)$ faces are pigmented or not. Several such instances were observed with smoky quartz. The general predominance in size of the colored set of sectors over the colorless set, as seen in section, reflects the general tendency of quartz to develop a habit in which $(10\bar{1}1)$ predominates over $(01\bar{1}1)$. Distorted crystals may yield sections with an unusual arrangement of sectors; some of the sections figured by Descloizeaux are remarkable in this respect. A section figured by Brewster which contains four colored and twinned sectors is presumably due to an accidental intergrowth of another crystal or to a twinned insert which happened to bring in an additional sector.

A segmental coloration is also found to occur occasionally in smoky quartz crystals. One of a group of sectioned smoky quartz crystals from Brazil, originally contained in the collection of the late George F. Kunz, exhibits an interior sectoral light brown coloration with a uniform border of a smoky color. The pigment is present in sharply marked color bands in each of the two portions, occurring in vertical planes parallel to $(10\bar{1}0)$ in the outer border and in planes parallel to a rhombohedron in the inner sectoral portion. A similar distribution of a smoky color was observed in a sectioned smoky quartz crystal from the Little Pipestone district, Jefferson Co., Montana. A pronounced segmental coloration beneath a set of rhombohedral faces, with color planes, is shown by a smoky crystal from New Zealand (Fig. 2). This crystal is enclosed within a larger crystal of colorless quartz which has been artificially rounded off and polished so that the base of the specimen, which is cut $\perp$ to c, and through which the segmental coloration is observed, does not possess a hexagonal outline. A segmental coloration beneath the faces of a terminating rhombohedron was also observed in light colored smoky quartz crystals from the Mourne Mts., Ireland, this being the only further instance of a segmental coloration of smoky quartz seen by the writer. The pigmented segments in all of these instances are beneath one of the two terminating rhombohedrons, the prism being also pigmented in two of the instances, but it was not possible in any of them to identify the particular rhombohedron responsible for the coloration. It is probable, however, that the pigmented faces are those of the positive rhombohedron, as this form is known to selectively include the pigment of amethyst and also other

foreign substances, to be mentioned shortly. Brewster has described a section exhibiting a yellowish sectoral coloration, an amethyst tint being lacking, in which the colored sectors are twinned in the fashion of amethyst. Twinning of the pseudo-racemic type, on the Brazil law, was not observed in any of the sectorally or uniformly colored sections of smoky quartz examined by the writer, but relatively simple twins on $(10\bar{1}0)$ were noted.

In a specimen of pale smoky quartz from Brazil it was noted that the color planes parallel to the terminating rhombohedrons were more deeply pigmented in the regions of these planes immediately adjacent to the edges between the rhombohedrons. In another specimen of Brazilian smoky quartz the color planes were observed to contain macroscopic particles of a white flocculent material (chalcedony ?) which were more abundant in the outermost growth or color planes of the crystal.

A segmental coloration is seemingly much less abundant with smoky quartz than with amethyst, with which variety it is very frequently met. Color planes parallel to the growth surfaces are of general occurrence in smoky quartz, however, with the exception of crystals from the Swiss localities. The color of these is usually evenly distributed.

ORIGIN OF THE SEGMENTAL COLORATION

Segmental colorations can be produced experimentally by growing crystals of alum and other substances from solutions containing a small amount of a suitable dye. The dye in these instances is adsorbed selectively by one of the forms bounding the crystal during its growth so that colored segments are formed subjacent to the faces of the adsorbing form, meeting at the center (nucleus) of the crystal, while the segments subjacent to the faces of the non-adsorbing form or forms remain uncolored. Such instances have been described by a number of writers and the phenomenon has been treated at length by France and co-workers (1930). A photograph of a segmentally colored alum crystal is given in Fig. 3. This phenomenon is the same as that of the modification of crystal habit by the selective adsorption of a foreign substance contained in the crystallizing solution and differs only in that the adsorbed substance is visible by reason of its color.

The well known hour-glass crystals of augite, so-called because of the two-fold divergent sectoral distribution of color as seen in section, have also been interpreted as resulting from the adsorption of TiO_2 or a colored titania-rich molecule by one of the growth forms of the crystal (Scott, 1914). A double hour-glass sectoral coloration has also been

described in a large torbernite crystal by Hallimond (1916). This crystal is bounded by (001), (101), (103) and (112) and is described as having the latter form selectively stained by the pigment (i.e., adsorbed) during the growth of the crystal, so that a basal cleavage section reveals colored or turbid sectors based upon the faces of this form and extending to the center while the other sectors are uncolored. Color bands are also shown by the crystal. Fluorite crystals possessing a segmental coloration have been described by Steinmetz (1925) who figures sections bounded by faces of (110) and (100) in which the pigment has been included during growth in the sectors based upon the latter form while the sectors based upon (110) are not pigmented. Drugman (1932) has described and figured fluorite dodecahedrons modified by small faces of the octahedron which possess six small localized patches of a violet color disposed internally in the direction of the four-fold axes of symmetry, each patch of color being located a little below the summit of the six corresponding four-fold corners of the crystal. These patches may represent small selectively pigmented faces of (100) originally present on the crystal and later overgrown. Kenngott (1854) has mentioned a green trisoctahedron of fluorite modified by narrow dodecahedral faces which are of a violet color and also another crystal of fluorite in which the three axial sections are colorless and the rest of the crystal violet blue. A specimen of fluorite, from Cornwall, in the collection of the American Museum, exhibits colorless cubes modified by faces of a tetrahexahedron which contain a zone or segment about 1 mm. thick of a deep purple color beneath them. Another specimen, also from Cornwall, exhibits fluorite crystals of a similar habit but in which the cube portion is of a light sea green color while very thin segments beneath the tetrahexahedral faces are of a light violet color. In both of these instances the crystals appear to have grown as simple cubes during the early stages of growth while the tetrahexahedron developed at a late stage of growth, the two forms then growing simultaneously with the tetrahexahedral faces selectively including a purple or violet pigment. A large deep amethyst colored fluorite crystal from Illinois contains an interior phantom of a cubo-octahedral habit which is visible, when the crystal is held against a source of light, by reason of the absence of pigment in the segments belonging to the octahedral faces. These segmentally colored fluorite crystals also appear to be the result of the selective adsorption of pigment by the forms of the growing crystal. Color planes are found in many colored fluorite crystals, whether segmentally colored or not. Further instances of the segmental coloration of crystals have been

described by Pelikan (1896) for augite, barite and other natural species and for artificially colored crystals of strontium nitrate.

In the case of amethyst and smoky quartz it is likewise believed that the segmental coloration described is due to the selective adsorption of the pigmenting substance[1] by the growth faces of the crystal. Of the three common forms the positive rhombohedron $(10\bar{1}1)$ is the most strongly adsorbing with the negative rhombohedron $(01\bar{1}1)$ less strongly adsorbing but more so than the prism $(10\bar{1}0)$, judging from the relative frequency of occurrence. The invariable continuity of the color planes parallel to the prism faces around the crystal reflects the identical structure and hence equal adsorbing power of the six faces of this form while the unequal adsorbing power of the two rhombohedral forms is in accordance with their different structures, as revealed by the difference in etch figures upon them and their different rates of growth and solution. The rate of solution is greater upon the negative rhombohedron than upon the positive rhombohedron while the prism is much more resistant to solution than either of these two forms. The rate of solution is greatest in the direction of the vertical axis. The prism seems to be in general the slowest growing of the three common forms, as is testified by the prismatic habit characteristic of the species.

This interpretation of the segmental coloration is, for amethyst, supported by the occurrence of quartz crystals whose surfaces are selectively filmed by iron oxide, this substance apparently being adsorbed from a sol which bathed the crystals after the completion of their growth. A suite of specimens from West Paterson, New Jersey, exhibits drusy surfaces of small colorless quartz crystals filmed over upon $(10\bar{1}1)$ or upon $(10\bar{1}1)$ and $(10\bar{1}0)$, the form $(01\bar{1}1)$ in all of the instances remaining unfilmed (Frondel, 1934*a*). The film varies between brownish red, red and brick red in color, and while thin is quite dense. It may be rubbed off, revealing the undersurface to be smooth and brilliant. Adsorption of the iron oxide during the growth of the crystal in these instances would presumably have resulted in the formation of a segmentally colored amethyst. Calcite crystals associated with the quartz crystals of these specimens are also selectively filmed over by iron oxide (Frondel, 1934*b*). A photograph of an amethyst crystal from Thunder Bay, Michigan, in the collection of the Illinois State Museum, whose surface is selectively filmed over by iron oxide, has been published by Crook

[1]Which for amethyst is known to be a compound of ferric iron (Holden, 1924), and is very probably colloidal hydrous iron oxide approaching goethite in composition.

(1920). This crystal[1] measures about 4½ by 4 inches, with a base of white quartz, and has three alternating faces filmed over by iron oxide, particularly towards the apical parts of these faces, while the other three faces are without indication of iron oxide. The three filmed faces are slightly larger than the three faces of the unfilmed form, which suggests that the former are those of the positive rhombohedron $(10\bar{1}1)$. A case in which a varnish-like coating of powdery rutile is selectively disposed upon the apical parts of three alternating rhombohedral faces of a Brazilian quartz crystal, the other three faces being uniformly covered, has been described by Brewster (1853). The identity of the forms in this instance is not known. Instances have also been described (Frondel, 1934*a*) of quartz crystals of which the faces of $(10\bar{1}1)$ have selectively adsorbed and included during the last stages of growth quantities of colloidal clay material, the faces of $(01\bar{1}1)$ being non-adsorbing. The $(10\bar{1}1)$ faces in these instances possess an enameled or pearly submetallic luster similar to that of the cotterite variety of quartz, which variety has similarly resulted from the (non-selective) inclusion of colloidal clay substance.

The observation frequently made, first apparently by Beck (1842), to the effect that the quartz crystals occurring in deposits of iron ore are characterized by the development of a bipyramidal habit, the prism being absent, is also of interest in this connection. It is found that the form of artficially grown crystals which adsorbs dyes or other substances tends to become the dominant habit of the crystal, since the action of the adsorption is to decrease the growth velocity of the form by cutting down the normal accretion on the surface, and, since the two terminating rhombohedrons of quartz are generally more strongly adsorbing for iron oxide than the prism, as is known from the adsorbing behavior of amethyst, a bipyramidal habit can be expected to develop on quartz crystals growing in such an environment. The $(10\bar{1}1)$ form of quartz is more strongly adsorbing for Ca ion than $(01\bar{1}1)$ and both $(10\bar{1}1)$ and $(01\bar{1}1)$ are more strongly adsorbing than $(10\bar{1}0)$, as is shown by the pseudocubic or bipyramidal habit developed by quartz occurring in gypsum deposits (Tarr, 1929; Tarr and Lonsdale, 1929).

A further point of interest in connection with amethyst lies in the fact that the segments of the crystal beneath the faces of $(10\bar{1}1)$, which is the most strongly adsorbing form, are generally those which contain the pseudo-racemic twinning characteristic of this variety of quartz, the

[1]A description of this specimen was kindly furnished by Mr. A. S. Coggeshall, Chief, State Museum Division, Department of Registration and Education, Illinois.

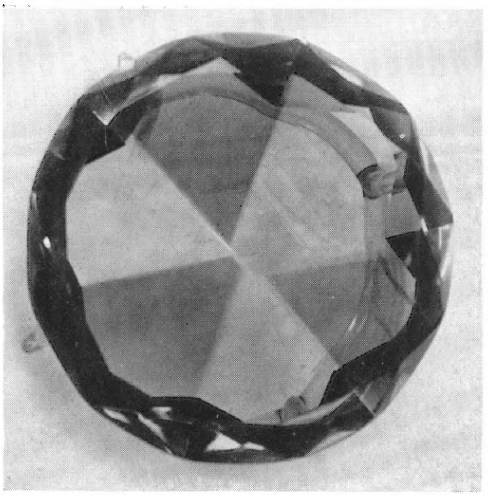
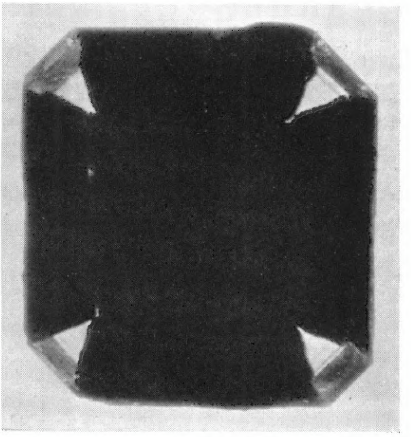


Fig. 1



W. G. France photo.

Fig. 3

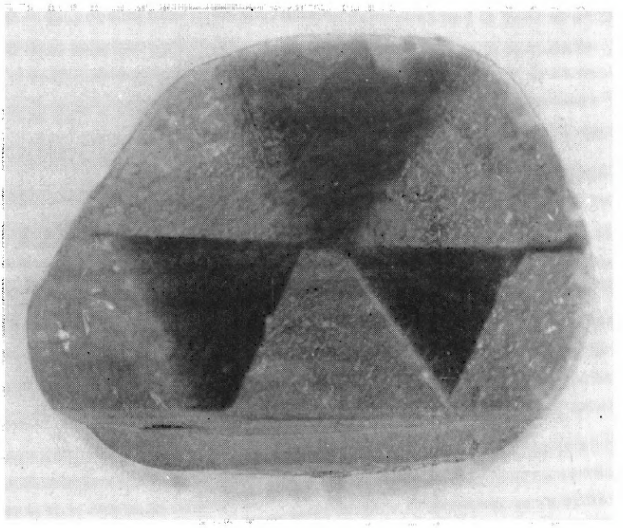


Fig. 2

Fig. 1. A cut amethyst with a sectoral coloration. The table of the stone is cut $\perp c$. Ceylon. (Morgan Gem Collection.)

Fig. 2. A sectorally colored smoky quartz crystal. The smoky crystal is enclosed in a larger crystal of colorless quartz the surface of which has been artificially rounded off. The section is $\perp c$. New Zealand.

Fig. 3. A double hour-glass segmental coloration produced by the adsorption of diamine sky blue at the (100) faces of an ammonium alum crystal. The segments beneath (111) are uncolored and their borders appear dark in the photograph only as the result of the reflection of the light from these surfaces.

other segments being untwinned or twinned once with the composition plane approximately bisecting the segment. The coincidence of the twinning and the selective coloration, beneath $(10\bar{1}1)$, of sections was first remarked on and figured by Brewster and has been noted by many of the later workers. Bunn (1933) has recently pointed out that a sort of mimetic twin structure is shown by the segments beneath the adsorbing faces of several artificial crystal species, as a consequence of the adsorption, and that anomalous birefringence may also be produced in crystals containing adsorbed impurities. Bunn states that sodium chlorate crystals selectively adsorb thiosulphate on the faces of the tetrahedron and that crystals composed of the cube and the tetrahedron exhibit anomalous birefringence in the segments subjacent to the faces of the latter form. From this it appears that the twinning of amethyst may be induced by the adsorption of the foreign substance causing the color, a view that has also been expressed by Mügge (1907) and others. Tutton (1911, 1924) and Judd (1888, 1893) ascribed a secondary origin to the twinning of amethyst and also to its color. The pleochroism of amethyst may be due to oriented adsorption.

SIGNIFICANCE OF THE SEGMENTAL COLORATION OF SMOKY QUARTZ AND OF VARICOLORED OVERGROWTHS

Holden (1925), in a notable paper, has advanced the theory that smoky quartz owes its color to the presence of colloidal particles of free silicon liberated by the action of radium radiation on an originally colorless crystal. The distribution of the pigment of smoky quartz in color planes and occasionally also in selectively pigmented segments, both of which are related to the growth surfaces, is, however, direct evidence of the inclusion of the pigment during the growth of the crystal. The fact that the pigmented regions of smoky quartz alternate with regions of colorless quartz is itself not compatible with Holden's theory, since a secondary pigment produced by the disintegration of the silica should be in uniform distribution throughout the crystal. The association by overgrowth of differently colored crystals of essentially the same period of formation also militates against the view of a secondarily produced color.

A specimen from Delaware County, Pennsylvania, in the collection of the American Museum, exhibits a large, doubly terminated bipyramidal crystal of smoky quartz with an interior phantom of amethyst quartz; other specimens from this locality show large crystals with an amethyst color in the segments subjacent to the faces of the two termi-

nating rhombohedrons and a smoky color in the segments subjacent to the faces of the prism.[1] A crystal from Pikes Peak, Colorado, is smoky towards the base and amethystine towards the apice, and somewhat similar specimens from Mt. Antero, Colo., show crystals towards the base of which smoky color planes surround a very faintly amethystine interior. The specimen shown in Fig. 2, from New Zealand, consists of a smoky phantom in a colorless quartz crystal, and similar occurrences were observed from Hot Springs, Arkansas. and Graubunden, Switzerland. A group of specimens from an unknown locality in Brazil exhibit amethyst phantoms in colorless quartz. Related to these occurrences are sceptre crystals of quartz which exhibit color differences. On finely developed crystals of this nature from Carlow, Ireland, the enlarged end is of a smoky color while the thinner supporting prism is of almost colorless quartz. On similar specimens from Monroe, Connecticut, and Alexander County, North Carolina, the enlarged portion is colorless, or almost so, and the thinner prism part of a pale smoky color. A sceptre quartz specimen from Sonora, Mexico, shows terminal amethystine enlargements of colorless prisms. Further evidence is afforded by specimens showing two generations of quartz as oriented overgrowths. Suites of specimens from the Little Pipestone district, Jefferson Co., Montana, and from the Pikes Peak region, Colo., exhibit overgrowths of amethyst crystals on smoky quartz crystals, and identical occurrences were observed on specimens from Switzerland (exact locality unknown); Amherst County, Virginia; and from Lincoln County, N. C. A specimen from Noyes Mtn., Greenwood, Maine, exhibits fine smoky crystals containing color bands overgrowing colorless to milky quartz. Amethyst crystals overgrowing colorless quartz crystals were observed on specimens from Schemnitz, Bohemia; Guanajuato, Mexico; and St. Gotthard, Switzerland. Specimens from Bear Creek, Colo., and Crystal Peak, Colo., consist of smoky crystals with an overgrowing layer of white opaque quartz. Wada (1904) mentions quartz crystals from a locality in Japan which present a zonal structure of colorless, smoky and sometimes amethyst layers. These colors are apparently all present in the same crystal although this is not directly stated. A zonal distribution of color (that is, in color planes) in crystals from another locality is described as consisting of a core of alternate layers of colorless and smoky quartz which is covered with an amethystine layer.

These features of association and color distribution are best ex-

[1]James Bruce, in 1813 (Amer. Miner. Jour., I, No. 4, p. 242) says that a Mr. Cloud of the United States Mint suggested that the color of the amethyst from this locality was due to titanium (oxide), a view also taken by Wherry (1904, Mineral Collector, XI, p. 88).

plained on the basis that the crystals included the pigmenting substance during their growth from the solution, the solution varying in its content of pigmenting substance, and, also, in the kind or kinds of pigmenting substance present, since if the color were a secondary one brought out by radiation, both generations of the crystals and all parts of a single crystal would be equally affected. Holden has argued on similar grounds that an occurrence described by him of gray quartz and rose quartz in juxtaposition casts doubt on the theory that rose quartz has a secondary color produced by the action of radium radiation on white quartz. Since silicon is unlikely to exist in the free state as a (colloidal) constituent of natural solutions, the question of the nature of the pigment in natural smoky quartz must be considered an open one. The smoky color produced in radiated colorless quartz may be colloidal free silicon, as thought by Holden and others, but the similarity in color between the natural and synthetic varieties must be considered as only accidental. Glass may be colored shades of yellow and brown both by the addition of carbon to the melt and by radiation.

Holden has stated in support of his thesis that smoky quartz is characteristically associated with radioactive minerals, but numerous occurrences are known without such an association. Whitlock (1905) has described an occurrence of smoky quartz at Rondout, Ulster Co., New York, where it is found as smoky crystals with strongly marked color planes and as smoky phantoms in colorless crystals in clay pockets in the Manlius limestone.[1] Small amounts of an anthracitic hydrocarbon occur in the limestone. The well known quartz crystals from localities in Herkimer County, N. Y., which occur in cavities in a carbonaceous Ordovician limestone, are generally perfectly transparent and colorless, but a suite of specimens in the American Museum possess a pale but quite definite smoky color. These crystals contain visible specks of a brilliant black anthracite-like hydrocarbon. Dana (1893) mentions smoky quartz as occurring at Little Falls, Herkimer Co., N. Y., where it is found with calcite and barite in the limestone. Beck (1842) says that the anthracitic hydrocarbon commonly associated with the quartz from this region of New York State is frequently diffused throughout the entire body of the crystal. Smoky quartz is also found occasionally associated with zeolites in the New Jersey diabase region, as at Great Notch, Paterson and West Paterson (Manchester, 1931), although the quartz from these localities is generally colorless or amethy-

[1]The writer is indebted to Dr. David H. Newland of the New York State Museum for an opportunity to examine some of these specimens.

stine, and it has been noted as occurring in crystalline limestone at Newton, New Jersey, associated with spinel, graphite, chondrodite, etc. Whitlock (1903) also notes occurrences of smoky quartz in crystalline metamorphic limestone at Kingsbridge, N. Y., and from near Port Henry, N. Y., associated with pyroxene, graphite and other species. Robinson (1825) mentions smoky quartz as occurring in cavities in trap rock at East Haven, Conn., associated with amethyst, chalcedony and analcite, and also dark smoke brown quartz as occurring in limestone near Quebec, the crystals from this locality being stated to contain in rare instances a drop of a pale bituminous liquid. Since there is no radiation available in these occurrences this would dispose of a theory to the effect that the distribution of color in planes parallel to the growth faces is due to the inclusion during growth of a colorless impurity which localized the action of the radiation.

The observation of Nutting (1931) that quartz surfaces adsorb unsaturated hydrocarbons with such intensity that they are "cracked," with the formation of free carbon, is of significance in this connection.

HISTORICAL NOTES ON THE PIGMENT OF AMETHYST

It is of interest to note that the color of amethyst was ascribed to iron (oxide) by John Woodward in 1729, who speaks of an occurrence of quartz as ". . . some of the crystals Red, others Amethystine; concreted on a crust of Iron-ore, growing on the side of a perpendicular fissure in St. Vincent's Rock, Bristol. These different colors are owing to the different Proportions of ferreous corpuscles uniting with the Crystalline in the Concretion." Woodward also notes an occurrence of cubic spar (fluorite ?) with a purple cast of color from a lead mine at Nenthead, Cumberland, and states that the color is owing to an infinitely small admixture of iron. Poggendorf (1841) is said to be the first to ascribe the color of amethyst to a compound of iron, but the idea had been already expressed not only by Woodward but also by Marx (1831), who believed that hydrated iron oxide was the pigmenting substance, and by Haüy (1817), who believed that the color of amethyst and all other gems, with the exception of emerald and spinel, was due to iron oxide. Brewster (1853) speaks of amethyst as having grown from "amethystine solutions."

J. F. Henckel, in 1725, thought that the color of amethyst might be due to (colloidal) gold: "In particular the violet cast of the amethist, and the red blush of the jasper, whereby it comes to resemble coral, would seem to suggest an enquiry, whether their tint be not owing to the

share of metal they contain. I know not, whether the amethist does not hold gold; as there is no experiment extant for giving such a violet colour to a stone, or stony glass-flux, except by the means of gold, with the addition of tin, especially as I have a method of imparting this colour to spring water, without making it less sweet and potable, . . . " Henckel is referring to the "Purple of Cassius." Elsewhere Henckel states that the red and brown colors of certain cryptocrystalline varieties of quartz are due to included iron oxide. Ebelmen, in 1847, produced amethystine, topaz-yellow and rose-colored hyalite and hydrophane by means of colloidal gold. His method was to precipitate silica gel from silicic ether mixed with an alcoholic solution of gold chloride and to expose the product to diffuse light or to the direct light of the sun. Diffuse light yielded topaz-yellow colors, and, with time, aventurine gels containing flaky gold; this seems to be a pigment color while the violet blue tints, which were obtained by the action of direct sunlight, are certainly structural colors. The aventurine gels were greenish by transmitted light. Holden (1924) obtained rose-colored silica gels by using manganese salts. Doelter (1909) produced synthetic rose quartz colored by colloidal gold by passing a current through a gilded quartz section held at a high temperature.

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